

NPS ARCHIVE  
1963  
PATTERSON, L.

INFRARED SPECTRUM OF BROMODIBORANE  
AND ATTEMPTED PREPARATION OF  
CHLORODIBORANE FOR INFRARED STUDY

LEE ROY PATTERSON

LIBRARY

U.S. NAVAL POSTGRADUATE SCHOOL  
MONTEREY, CALIFORNIA









INFRARED SPECTRUM OF BROMODIBORANE  
AND ATTEMPTED PREPARATION OF CHLORODIBORANE  
FOR INFRARED STUDY

\* \* \* \* \*

Lee Roy Patterson





INFRARED SPECTRUM OF BROMODIBORANE  
AND ATTEMPTED PREPARATION OF CHLORODIBORANE  
FOR INFRARED STUDY

by

Lee Roy Patterson

Lieutenant, United States Navy

Submitted in partial fulfillment of  
the requirements for the degree of

MASTER OF SCIENCE  
IN  
CHEMISTRY

United States Naval Postgraduate School  
Monterey, California

1963

NPS Archive  
1963  
Patterson, L.

~~Niesjs~~  
~~D 67~~

INFRARED SPECTRUM OF BROMODIBORANE  
AND ATTEMPTED PREPARATION OF CHLORODIBORANE  
FOR INFRARED STUDY

by

Lee Roy Patterson

This work is accepted as fulfilling  
the thesis requirements for the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

from the

United States Naval Postgraduate School

---



## ABSTRACT

Bromodiborane,  $B_2H_5Br$ , was prepared by mixing bromine and diborane. The resulting unstable  $B_2H_5Br$  was separated from its equilibrium mixture by standard fractionation techniques in a high vacuum system. The infrared spectrum in the  $4000$  to  $250\text{ cm}^{-1}$  region was obtained for  $B_2H_5Br$  in both the gaseous state and as a frozen solid film. Frequency assignments were made by correlation with  $B_2H_5D$  and  $B_2H_5CH_3$  assignments.

The preparation of chlorodiborane,  $B_2H_5Cl$ , was attempted by mixing  $BCl_3$  and  $B_2H_6$ . All attempts to separate  $B_2H_5Cl$  from its equilibrium mixture were unsuccessful as were all attempts to observe its formation by absorption spectrum of the gas mixture.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor J. W. Schultz of the U. S. Naval Postgraduate School in these investigations.



## TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION	1
II	EXPERIMENTAL METHODS	2
	1. Preparation of Diborane	2
	2. Attempted Preparation of Chlorodiborane	7
	3. Preparation of Bromodiborane	11
	4. Infrared Spectrum of $B_2H_5Br$	15
III	INTERPRETATION OF INFRARED SPECTRUM OF $B_2H_5Br$	24
	1. Symmetry of $B_2H_5Br$	24
	2. Frequency Assignments	27
IV	DISCUSSION OF RESULTS	30
V	BIBLIOGRAPHY	32





# LIST OF ILLUSTRATIONS

FIGURE		PAGE
1.	Initial method of producing $B_2H_6$	3
2.	Primary method of producing $B_2H_6$	5
3.	Comparison of $B_2H_5Br$ spectra when pure and after decomposing for an hour at room temperature	18
4.	Comparison of $B_2H_6$ and $B_2H_5Br$ spectra	19
5.	$B_2H_5Br$ spectrum on expanded scale	20
6.	$B_2H_5Br$ spectrum in cesium bromide region	21
7.	$B_2H_5Br$ spectrum as solid film	22
8.	$B_2H_5Br$ spectrum as solid film	23
9.	The character of the normal vibrations of "bridge" diborane	25
10.	Correlation of frequencies for terminally substituted diborane	28



## I. INTRODUCTION

The vibrational spectra of  $B_2H_6$  and  $B_2D_6$  are well understood and relatively little doubt remains regarding assignments of fundamentals./1-4/ The effects on the vibrational spectrum of diborane when deuterium is substituted for one of the terminal protium atoms /5/ and the effects of  $CH_3-$  and  $C_2H_5-$  groups substituted on diborane /6/ have led to the assignment of some bands believed to be caused by the  $-B_2H_5$  fragment./6/ The examination of spectra of the halodiboranes ( $B_2H_5Cl$  and  $B_2H_5Br$ ) would be a further check on the assignments given for the  $-B_2H_5$  fragment and should assist ultimately in elucidating structures of more complex boron hydrides.



## II. EXPERIMENTAL METHODS

### 1. Preparation of diborane.

Preparation of a monohalogen-substituted diborane requires the preparation of the intermediate, diborane, itself. The procedure first used for producing diborane was that suggested by R. Turner. /7/ Six grams of powdered potassium borohydride,  $\text{KBH}_4$ , (97% pure obtained from Metal Hydrides Company, Beverly, Mass.) were placed in a 500 milliliter three necked flask equipped with a magnetic stirrer. (Fig. 1) Through one neck passed dried hydrogen gas. The gases evolved were emitted through another neck. Through the third neck, 4N  $\text{H}_2\text{SO}_4$  was allowed to drop onto the powdered  $\text{KBH}_4$ . The reaction was quite vigorous and was essentially complete after the addition of about 40 ml of acid, but 250 ml in all were added to insure completion. The gases given off were passed through a dry ice cooled trap and then a liquid air cooled trap where the product was collected. The non-condensed gases were allowed to pass through a mercury bubbler under a hood.

During thirteen such processes in which the acid dropping rate, the stirring rate, the sweeping gas rate and the temperature of the reaction were all varied, the yield of pure  $\text{B}_2\text{H}_6$  as established by infrared spectrum never exceeded three percent. Along with the poor yield there was generally a high contamination due to  $\text{CO}_2$  in the product gases. In fact, the percent contamination rose irregularly with each experiment. All evidence pointed to the  $\text{KBH}_4$  actually containing some carbonate as an impurity. The  $\text{KBH}_4$  evidently absorbed

Vol. 71, Part 1, 1941. Published by the Royal Anthropological Institute, 21, BEDFORD SQUARE, LONDON, W.C.2.

CONTENTS

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 1. PAGES 1-100.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 2. PAGES 101-200.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 3. PAGES 201-300.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 4. PAGES 301-400.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 5. PAGES 401-500.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 6. PAGES 501-600.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 7. PAGES 601-700.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 8. PAGES 701-800.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 9. PAGES 801-900.

THE JOURNAL OF THE ROYAL ANTHROPOLOGICAL INSTITUTE, 1941. PART 10. PAGES 901-1000.

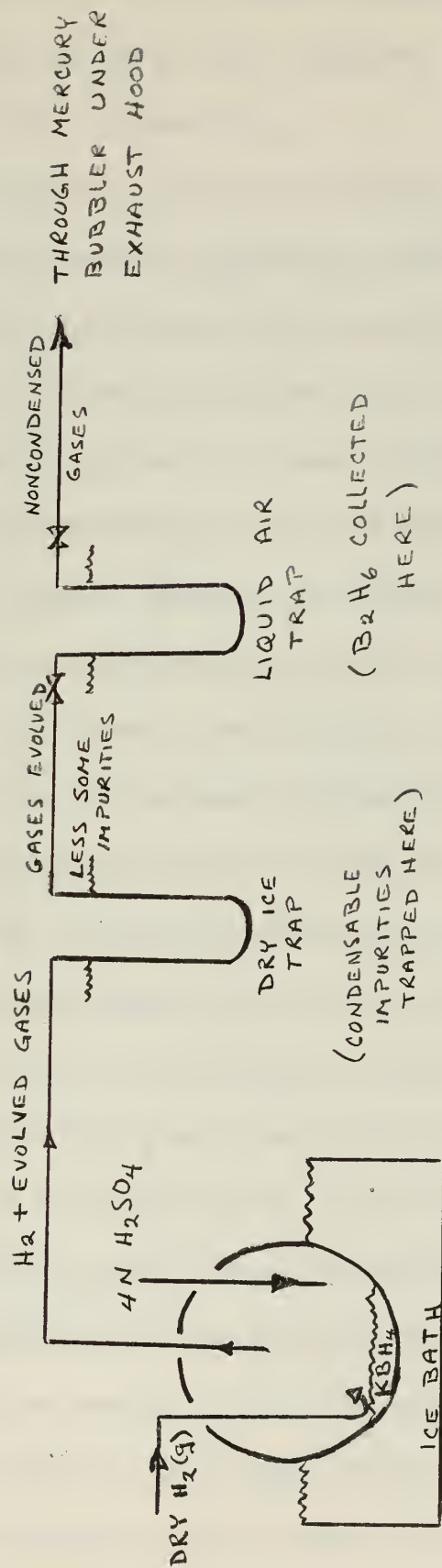


Fig. 1. Initial Method of Producing  $B_2H_6$

4N  $H_2SO_4$  Added to Solid  $KBH_4$





$\text{CO}_2$  and moisture from the air each time the  $\text{KBH}_4$  container was opened, and the borohydride reacted to form a carbonate. The carbonate in turn reacted with the acid to liberate  $\text{CO}_2$ .

In analyzing the poor yield for the reaction, it was decided that the highly exothermic reaction caused much steam to form from the 4N acid, and this steam hydrolyzed the  $\text{B}_2\text{H}_6$  rapidly to form  $\text{B}(\text{OH})_3 + \text{H}_2$ . No matter how slow the reaction, or how cool, the hydrolysis destroyed the majority of the  $\text{B}_2\text{H}_6$  formed. The only modification to the reaction that could solve the problem was to use concentrated  $\text{H}_2\text{SO}_4$  and eliminate the water; however, dropping concentrated  $\text{H}_2\text{SO}_4$  onto solid  $\text{KBH}_4$  -- even in an inert atmosphere of helium -- was far too vigorous a reaction to be safely done in the laboratory. The concentrated acid plus borohydride approach had been published /8/ though with the recommended modification that the solid  $\text{KBH}_4$  be added slowly and in small amounts to the concentrated sulfuric acid instead of vice versa.

Since the original yields were so low, a switch was made to the new procedure of adding the solid  $\text{KBH}_4$  to the acid. Two hundred milliliters of concentrated  $\text{H}_2\text{SO}_4$  were placed into a 500 ml three necked flask equipped with a magnetic stirrer. (Fig. 2) One neck still contained the sweeping gas inlet, but the sweeping gas now utilized was dried helium. The second neck was attached to a cold finger condenser containing dry ice and acetone. The product gases passed by the cold finger condenser through a trap at about  $-130^\circ\text{C}$  (ligroin at its melting point) and were collected in a trap at liquid air temperature. Any



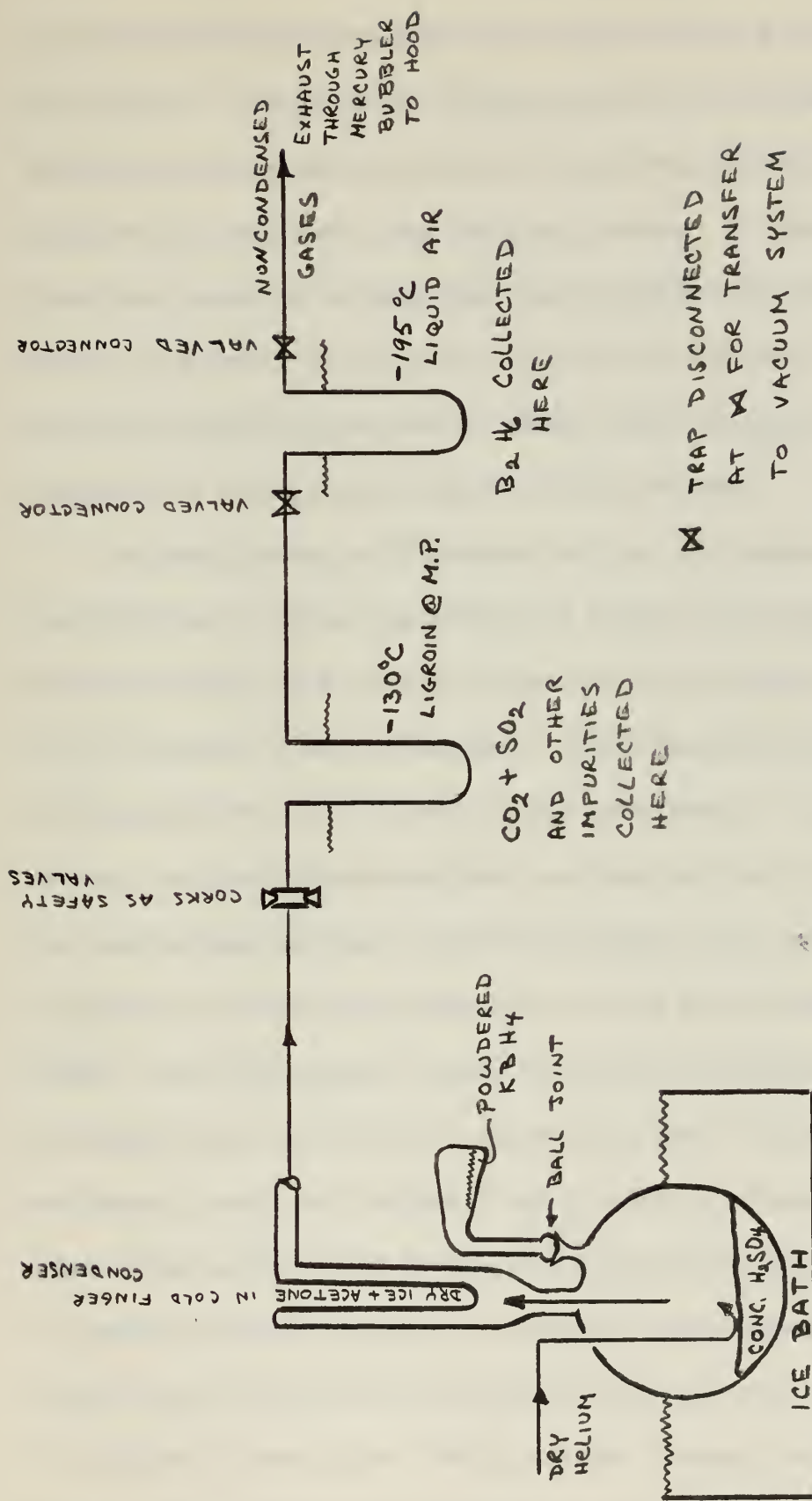


Fig. 2. Primary Method of Producing  $B_2H_6$

Solid  $KBH_4$  Added to Concentrated  $H_2SO_4$



1. The first part of the document is a list of items, each preceded by a number. The items are listed in a vertical column on the left side of the page. The numbers are 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.

noncondensable gases were allowed to pass through a mercury bubbler into a hood. The cold finger condenser plus the  $-130^{\circ}\text{C}$  trap were fairly effective in eliminating the previous  $\text{CO}_2$  contamination, but small amounts still persisted in the collected product. To the third neck of the flask was connected an Erlenmyer flask equipped with a tube at right angle to the flask. The tube was connected to the neck of the reaction flask via a ball joint and socket. Seven grams of  $\text{KBH}_4$  powder and a magnetic rod were placed inside the Erlenmyer flask.

By manipulating the Erlenmyer flask via the freedom of the ball joint while at the same time moving the magnet in the powder, small amounts of  $\text{KBH}_4$  were allowed to drop into the acid (which was cooled by an ice bath to slow the reaction). While the control of the rate of solid addition was not too good, it was satisfactory. In spite of the cooling, stirring, inert atmosphere, and slow addition of reactant, the reaction was extremely vigorous with some small amount of burning, or flashing, accompanying production of many fine particles of free sulfur. The sulfur rapidly covered the inside of the reaction flask and prevented visual observation of the reaction rate. The whole system was under a pressure of helium of about five psig. The decision as to when to add another small portion of solid could be made by watching the pressure gauge fluctuate as the product gases were evolved. The reaction was so rapid that the pressure often rose three to four psi upon the addition of some solid. During several of these preparations of  $\text{B}_2\text{H}_6$ , the pressure rose on the system sufficiently to blow out some





corks installed in the outlet line as safety valves. The addition of solid  $\text{KBH}_4$  to concentrated  $\text{H}_2\text{SO}_4$  consistently gave yields of about 50%  $\text{B}_2\text{H}_6$ , and this method was utilized for the preparation of all the  $\text{B}_2\text{H}_6$  used thereafter.

The  $\text{B}_2\text{H}_6$  that was collected in the liquid air cooled trap contained the impurities  $\text{SO}_2$  and  $\text{CO}_2$  in large quantities. The  $\text{B}_2\text{H}_6$  was purified by repeated fractional crystallizations in a vacuum system. This process was accomplished by detaching the liquid air cooled collecting trap from the preparation system as shown in Fig. 1 and reconnecting the still frozen trap to the vacuum system. Once the trap was integral to the vacuum system, the product gas,  $\text{B}_2\text{H}_6$ , was separated by repeatedly passing the gas mixture through traps at  $-76^\circ\text{C}$ ,  $-95^\circ\text{C}$ ,  $-130^\circ\text{C}$  and  $-195^\circ\text{C}$ . The  $\text{B}_2\text{H}_6$  was collected in the  $-195^\circ\text{C}$  trap as condensed vapor out of the  $-130^\circ\text{C}$  trap.

## 2. Attempted preparation of chlorodiborane.

Once an ample supply of  $\text{B}_2\text{H}_6$  was available, attempts to produce  $\text{B}_2\text{H}_5\text{Cl}$  were commenced. The chosen approach to preparing  $\text{B}_2\text{H}_5\text{Cl}$  was essentially that of Schlesinger and Burg /9/ in which freshly prepared  $\text{B}_2\text{H}_6$  is placed into a container containing  $\text{BCl}_3$  in near stoichiometric amounts according to:  $5\text{B}_2\text{H}_6 + 2\text{BCl}_3 = 6\text{B}_2\text{H}_5\text{Cl}$ . Since Schlesinger and Burg /10/ reported an equilibrium situation and fairly rapid kinetics such that it is nearly impossible to separate pure  $\text{B}_2\text{H}_5\text{Cl}$ , the plan was to place the  $\text{B}_2\text{H}_6$  and  $\text{BCl}_3$  into a standard IR gas cell and follow the process of the equilibrium and the formation of  $\text{B}_2\text{H}_5\text{Cl}$  by observing





the absorption spectrum of the gas mixture. Resolution of the  $B_2H_5Cl$  was to be accomplished by external compensation for the  $B_2H_6$  present in the mixture.

In the first attempt, about 70 mm<sup>1</sup> of  $BCl_3$  (obtained from Matheson Co., Inc., Newark, Calif.) along with 50 mm of  $B_2H_6$  were placed into a ten centimeter long pyrex glass IR gas cell and periodic spectra were taken to observe the reaction. Three new characteristic absorption peaks (3200, 1460, and 1360  $Cm^{-1}$ ) were found; however, upon evacuation of the cell, these peaks persisted on the inner surface of the NaCl windows of the cell. One hundred millimeters of  $BCl_3$  were placed into the cell by itself and the 3200 and 1460  $Cm^{-1}$  peaks were observed to decrease in intensity while the 1360  $Cm^{-1}$  peak increased. Furthermore, upon evacuation of the cell and then filling with 50 mm  $B_2H_6$  the opposite occurred -- the 3200 and 1460  $Cm^{-1}$  peaks increased as the 1360 peak decreased. Upon dismantling the empty IR cell, there was observed what appeared to be a reaction product from the beeswax and resin used to hold the NaCl windows in place on the glass cell.

To get away from the beeswax and resin interaction with the reactants, the whole process was tried again utilizing IR-tran windows and neoprene "O" rings as seals. The results were quite similar to the time before, only this time the "O" rings were being attacked instead of the wax and resin.

<sup>1</sup>All gas quantities are referred to by the pressure in the vessel considered in units of millimeters of mercury at room temperature. Usual vessel size was about 500 ml.



The idea of trying to watch the reaction as it took place in an IR cell was abandoned. It was decided to place the reactants into a 500 ml pyrex bulb sealed with a stopcock using relatively non-reactive Kel-F grease. The intention was to periodically transfer the contents of the reaction bulb to an IR cell for a few minutes and then transfer the gases back and hope that the time within the IR cell would be insufficient for the surface reaction previously observed to take place. Accordingly, 20 mm  $B_2H_6$  and 30 mm  $BCl_3$  were placed into the bulb. The bulb was placed in a  $0^\circ C$  bath for three hours to hold the  $BCl_3$  in liquid form. After the three hours, the bulb pressure had increased from 50 mm to 68 mm, and the IR spectrum showed some HCl formed and some decrease of  $B_2H_6$ . Also, 13 mm of the 68 mm total were noncondensable at liquid air temperatures -- presumed hydrogen. Then the amount of each reactant in the bulb was increased to 110 mm  $B_2H_6$  and 122 mm  $BCl_3$ , and the  $0^\circ C$  bath was repeated for four hours. This time there was a pressure increase to 350 mm, and 160 mm of noncondensable (in liquid air) gas was formed. There was some white solid formed in the vicinity of the region occupied by the liquid  $BCl_3$  (when at  $0^\circ C$ ). Again the IR spectrum showed a decrease in both reactants, but the only observable product in the spectrum was HCl. Of course, there was also the  $H_2$  gas and the solid formed. An IR spectrum of the solid showed it to be predominantly  $B(OH)_3$ . This would indicate that moisture managed to leak into the bulb and hydrolyze the  $B_2H_6$  accounting for the decrease in  $B_2H_6$  concentration. It was decided to try one more attempt to



produce an equilibrium mixture of  $B_2H_5Cl$ , but this time there was added to the old mixture (now mostly  $HCl$  in the bulb at a pressure of 190 mm) another 66 mm of  $BCl_3$  and 90 mm of  $B_2H_6$ . Then the bulb was subjected to a  $70^{\circ}C$  warm bath for six hours, and the mixture was checked by IR spectrum. There was some small decrease in both  $BCl_3$  and  $B_2H_6$  concentrations and 40 mm of noncondensable (presumed hydrogen) were formed; however, no new product was noticeable in the spectrum. Then the bulb with its gaseous mixture of about 50 mm  $BCl_3$ , 75 mm  $B_2H_6$  and 200 mm  $HCl$  was placed into another  $0^{\circ}C$  cold bath. After four hours of cold bath treatment, the gas mixture was again placed into an IR cell for a spectrum reading. The spectrum again showed a decrease in both  $B_2H_6$  and  $BCl_3$  with a small increase in  $HCl$ . No new peaks were noticeable. In all the attempts to produce  $B_2H_5Cl$ , an IR spectrum was used to "isolate" the  $B_2H_5Cl$ , and evidently if any  $B_2H_5Cl$  was produced it was in such small quantity relative to the  $B_2H_6$  present that its absorption spectrum was overshadowed by that of the  $B_2H_6$ .

An attempt was also made to use vapor phase chromatography (GLPC) to detect any new component, but no one column was found that would detect  $B_2H_6$ ,  $BCl_3$  and  $HCl$  at one time. The most nearly successful GLPC column was a 55 cm by 0.6 cm diameter tubing packed with 30 - 60 mesh firebrick with mineral oil as the adsorbing agent. /11/ With this column operating at room temperature and 2.5 PSI,  $B_2H_6$  was detected at an elapsed time of about 20 seconds. One GLPC run on

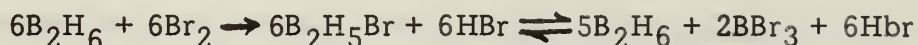




the final  $B_2H_6$ ,  $BCl_3$ ,  $HCl$  mixture detected a two percent yield of unknown gas (percentage based on  $B_2H_6$  plus unknown equal 100) at an elapsed time of about 25 seconds, or just after the  $B_2H_6$ . This unknown gas was definitely not  $HCl$  or  $BCl_3$  which were not detected within any reasonable time by the column. Whether this two percent was the elusive  $B_2H_5Cl$  was impossible to tell since the quantity was too small to collect to analyze by IR or chemical means. It was decided to abandon the attempt to produce  $B_2H_5Cl$  in favor of producing the more stable  $B_2H_5Br$ .

### 3. Preparation of bromodiborane.

The planned method of preparing  $B_2H_5Br$  was that specified by Stock /9/ in which  $B_2H_6$  and either  $HBr$  or  $Br_2$  are heated together for about two hours until the substitution is complete. In the case of the  $B_2H_5Br$  though, the compound is stable enough and sufficiently different in vapor pressure to allow separation from its equilibrium mixture -- believed to be: /9,10/



In the first attempt to produce  $B_2H_5Br$ , the method of warming equal volumes of  $HBr$  and  $B_2H_6$  at  $90^\circ C$  for two hours was chosen. /9/ Approximately 100 mm each of freshly prepared  $B_2H_6$  and the middle fraction of some commercially bottled  $HBr$  were placed in a 500 milliliter glass bulb. This bulb was placed into a hot bath for two hours, and then the contents were transferred to an IR cell for a spectrum. There was no noticeable change in the gas mixture except that two





millimeters pressure of noncondensable gas was formed. After transferring the gases back to the bulb, the bulb was heated at 90°C for another four hours. This time there was a reaction. However, it appeared that the major reaction was the result of heat causing the grease on the bulb's stopcock to thin sufficiently to allow air and water vapor to enter, since there was a deposit of white solid left on the inside of the bulb that later proved to be  $B(OH)_3$  according to an IR spectrum. There was also 96 mm of noncondensable gas that probably consisted of air plus  $H_2$  from the reaction  $B_2H_6 + 6H_2O = 2B(OH)_3 + 6H_2$ .

For the second attempt to produce  $B_2H_5Br$ , the method chosen was the alternate method recommended by Stock /9/ in which a one third stoichiometric amount of  $Br_2$  is added to  $B_2H_6$  and heated at 100°C till the  $Br_2$  color disappears. The reaction being  $B_2H_6 + Br_2 \rightarrow B_2H_5Br + HBr$ . Accordingly, 180 mm of  $B_2H_6$  were placed into a 500 ml glass bulb equipped with a well greased stopcock, and then 61 mm pressure of  $Br_2$  was added. Once again there was moisture contamination, but this time the stopcock was tight, and the moisture probably entered in accompaniment with the bromine. The  $Br_2$  vapor had been taken off of some liquid bromine via a vacuum system at room temperature without any fractionating. Evidently there was enough moisture present in the liquid bromine to be transferred over at room temperature with the bromine vapor. Anyway, the now familiar result



of hydrolyzed  $B_2H_6$  yielding the white solid  $B(OH)_3$  plus hydrogen was observed.

After cleaning the 500 ml reaction bulb for another try at producing  $B_2H_5Br$ , 284 mm pressure of  $B_2H_6$  was placed into the bulb along with 72 mm of carefully fractionated bromine vapor. Taking special precautions to insulate the stopcock from the heat of the  $100^\circ C$  bath, the mixture was heated for thirty minutes at which time the bromine color had disappeared. After transferring the gases from the reaction bulb to the vacuum system, it was found that about 30 mm of hydrogen had been formed. Fractionation of the remaining gases resulted in 10 mm pressure being isolated between temperatures of  $-130^\circ C$  and  $-30^\circ C$ . An IR spectrum of this 10 mm pressure in a 500 ml volume resulted in a logical spectrum for  $B_2H_5Br$ . No  $HBr$  appeared in the spectrum containing  $B_2H_5Br$ , but  $HBr$  was found in the fraction between  $-190^\circ C$  and  $-130^\circ C$  confirming a substitute reaction and effective fractional separation. To confirm the identity of  $B_2H_5Br$ , a vapor pressure reading was desired, and therefore more product was required. The original 10 mm of  $B_2H_5Br$  was frozen in liquid air, and the remaining gases from the original mixture were allowed to come to equilibrium again in the 500 ml reaction bulb. This time no heat was applied, the reaction bulb remaining at room temperature. Twenty four hours later, another ten millimeters pressure of  $B_2H_5Br$  in a volume of 500 ml was collected from the equilibrium mixture by fractional condensations on the vacuum system between baths of  $-130^\circ C$  and  $-30^\circ C$ . An IR spectrum of this



fraction was identical with the previous sample. This product was frozen with the previous sample and saved in an evacuated tube kept at liquid air temperature. Still the total amount of  $B_2H_5Br$  collected was insufficient to obtain a positive vapor pressure and confirm the sample as monobromodiborane. Consequently, another 115 mm pressure of carefully fractionated bromine plus 110 mm pressure of diborane was added to the previous equilibrium mixture in the 500 milliliter pyrex reaction bulb. A trace of bromine color persisted in the flask even after 48 hours at room temperatures, but heating the flask to  $70^{\circ}C$  for twenty minutes caused all color to disappear. Following the same separation techniques that produced the other two samples of ten millimeters pressure in a volume of 500 milliliters, a pressure of 18 millimeters of  $B_2H_5Br$  was obtained. After checking the spectrum of the third sample with that of the previous two, the three samples were combined. The reaction vessel was warmed at  $70^{\circ}C$  to speed the kinetics of the reaction back toward equilibrium during the time between separations of the  $B_2H_5Br$  from the equilibrium mixture. Three more fractions of total pressure of 36 millimeters in a 500 milliliter volume were separated from the mixture. In all, a total of 74 millimeters pressure of  $B_2H_5Br$  was collected in a 500 milliliter volume. This quantity was ample for checking vapor pressure, and the resulting vapor pressure of 42 mm at  $-44^{\circ}C$  agreed exactly with that found by Schlesinger and Burg /10/ and predicted by Stock. /9/ Another vapor pressure check gave a pressure of 95 mm at  $-30^{\circ}C$  and also agreed exactly with Stock's value. /9/

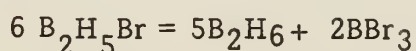


The first of these is the fact that the  
the second is the fact that the  
the third is the fact that the  
the fourth is the fact that the  
the fifth is the fact that the  
the sixth is the fact that the  
the seventh is the fact that the  
the eighth is the fact that the  
the ninth is the fact that the  
the tenth is the fact that the  
the eleventh is the fact that the  
the twelfth is the fact that the  
the thirteenth is the fact that the  
the fourteenth is the fact that the  
the fifteenth is the fact that the  
the sixteenth is the fact that the  
the seventeenth is the fact that the  
the eighteenth is the fact that the  
the nineteenth is the fact that the  
the twentieth is the fact that the  
the twenty-first is the fact that the  
the twenty-second is the fact that the  
the twenty-third is the fact that the  
the twenty-fourth is the fact that the  
the twenty-fifth is the fact that the  
the twenty-sixth is the fact that the  
the twenty-seventh is the fact that the  
the twenty-eighth is the fact that the  
the twenty-ninth is the fact that the  
the thirtieth is the fact that the  
the thirty-first is the fact that the  
the thirty-second is the fact that the  
the thirty-third is the fact that the  
the thirty-fourth is the fact that the  
the thirty-fifth is the fact that the  
the thirty-sixth is the fact that the  
the thirty-seventh is the fact that the  
the thirty-eighth is the fact that the  
the thirty-ninth is the fact that the  
the fortieth is the fact that the  
the forty-first is the fact that the  
the forty-second is the fact that the  
the forty-third is the fact that the  
the forty-fourth is the fact that the  
the forty-fifth is the fact that the  
the forty-sixth is the fact that the  
the forty-seventh is the fact that the  
the forty-eighth is the fact that the  
the forty-ninth is the fact that the  
the fiftieth is the fact that the  
the fifty-first is the fact that the  
the fifty-second is the fact that the  
the fifty-third is the fact that the  
the fifty-fourth is the fact that the  
the fifty-fifth is the fact that the  
the fifty-sixth is the fact that the  
the fifty-seventh is the fact that the  
the fifty-eighth is the fact that the  
the fifty-ninth is the fact that the  
the sixtieth is the fact that the  
the sixty-first is the fact that the  
the sixty-second is the fact that the  
the sixty-third is the fact that the  
the sixty-fourth is the fact that the  
the sixty-fifth is the fact that the  
the sixty-sixth is the fact that the  
the sixty-seventh is the fact that the  
the sixty-eighth is the fact that the  
the sixty-ninth is the fact that the  
the seventieth is the fact that the  
the seventy-first is the fact that the  
the seventy-second is the fact that the  
the seventy-third is the fact that the  
the seventy-fourth is the fact that the  
the seventy-fifth is the fact that the  
the seventy-sixth is the fact that the  
the seventy-seventh is the fact that the  
the seventy-eighth is the fact that the  
the seventy-ninth is the fact that the  
the eightieth is the fact that the  
the eighty-first is the fact that the  
the eighty-second is the fact that the  
the eighty-third is the fact that the  
the eighty-fourth is the fact that the  
the eighty-fifth is the fact that the  
the eighty-sixth is the fact that the  
the eighty-seventh is the fact that the  
the eighty-eighth is the fact that the  
the eighty-ninth is the fact that the  
the ninetieth is the fact that the  
the ninety-first is the fact that the  
the ninety-second is the fact that the  
the ninety-third is the fact that the  
the ninety-fourth is the fact that the  
the ninety-fifth is the fact that the  
the ninety-sixth is the fact that the  
the ninety-seventh is the fact that the  
the ninety-eighth is the fact that the  
the ninety-ninth is the fact that the  
the hundredth is the fact that the

#### 4. Infrared Spectrum of B<sub>2</sub>H<sub>5</sub>Br.

The infrared absorption spectrum was measured over the range 250 -- 4000 cm<sup>-1</sup> by means of a Perkin - Elmer Model 221 spectrophotometer equipped with CsBr and NaCl prism-grating interchanges. The instrument was equipped with a housing so that it could be swept out with dry nitrogen. In this way the effect of water vapor absorption on the spectra was reduced to a minimum. In the low frequency region (250 -- 650 cm<sup>-1</sup>), the CsBr prism was used, while the NaCl prism was used for the higher region. The resolution achieved was approximately uniform throughout the spectrum at about three cm<sup>-1</sup>. The band maxima were measured with a precision of about three cm<sup>-1</sup>. The gas absorption cells used were two cells ten cm in length with NaCl windows on one and CsBr windows on the other. Another five cm long micro gas cell equipped with IR-tran windows was used to resolve some weak bands.

The stability of the B<sub>2</sub>H<sub>5</sub>Br in the gas phase at room temperature was such that products of dissociation were noticeable as shoulders or small pips in the infrared spectrum after about thirty minutes. (See Fig. 3) Consequently, each gas phase spectrum required fresh separation of B<sub>2</sub>H<sub>5</sub>Br from its dissociation products. The change in the spectrum corresponding to the formation of B<sub>2</sub>H<sub>6</sub> and BBr<sub>3</sub>, the dissociation appeared to follow that reported by Schlesinger and Burg: /10/







The solid  $B_2H_5Br$  spectrum was obtained from a film of  $B_2H_5Br$  frozen onto a CsBr window held at liquid air temperature by a brass holder being in intimate contact with both the window and the liquid air. The brass holder and its window were enclosed in an evacuated cell also equipped with CsBr windows. The results of the absorption measurements are presented in Figs. 3 through 8 and Table I.

THE UNIVERSITY OF CHICAGO  
LIBRARY  
540 EAST 57TH STREET  
CHICAGO, ILL. 60637  
TEL. (312) 937-1234  
FAX (312) 937-1234  
WWW.CHICAGO.EDU

TABLE I. Table of frequencies of  $B_2H_5Br$  bands and their assignments

Frequency, $Cm^{-1}$ (Gas $B_2H_5Br$ )	Intensity	Frequency $Cm^{-1}$ (Solid $B_2H_5Br$ )	Intensity	Assignment
2618	Strong	2610	Strong	{ B-H asym., inphase (type B)
2603	Strong			
2580	Strong	2582	Strong	{ B-H asym., out of phase (type A)
2532	Strong	2518	Strong	{ B-H sym., in phase type B
2516	Strong			
2496	Weak			$B_2H_6$ impurity
		2440	Very Strong	?
2340	Very Weak	2358	Medium	?
		2333	Very Weak	?
		2282	Very Weak	?
1727	Weak	1727	Medium	B-H <sup>1</sup> asym., out of phase (type A)
1621	Medium	1620	Very Weak	$B_2H_6$ impurity
		1580	Very Strong	{ B-H <sup>1</sup> asym., in phase
1572	Very Strong			
		1554	Strong Shoulder	?
1540	Medium Shoulder			?
1488	Medium	1488	Very Strong	$-B_2H_5$ com- bination
		1445	Medium	?
1174	Weak			$B_2H_6$ impurity
1155	Weak			$BH_2$ deformation (?)
		1142	Very Strong	?
1064	Medium			{ $BH_2$ deformation
1049	Medium			
		1042	Very Strong	?
		941	Weak	?
934	Weak			?
904	Weak	905	Strong	$BH_2$ wagging, out of plane
817	Weak	816	Strong	$BH_2$ wagging in plane
661	Strong	659	Strong	?
496	Strong	496	Strong	B-Br Stretch



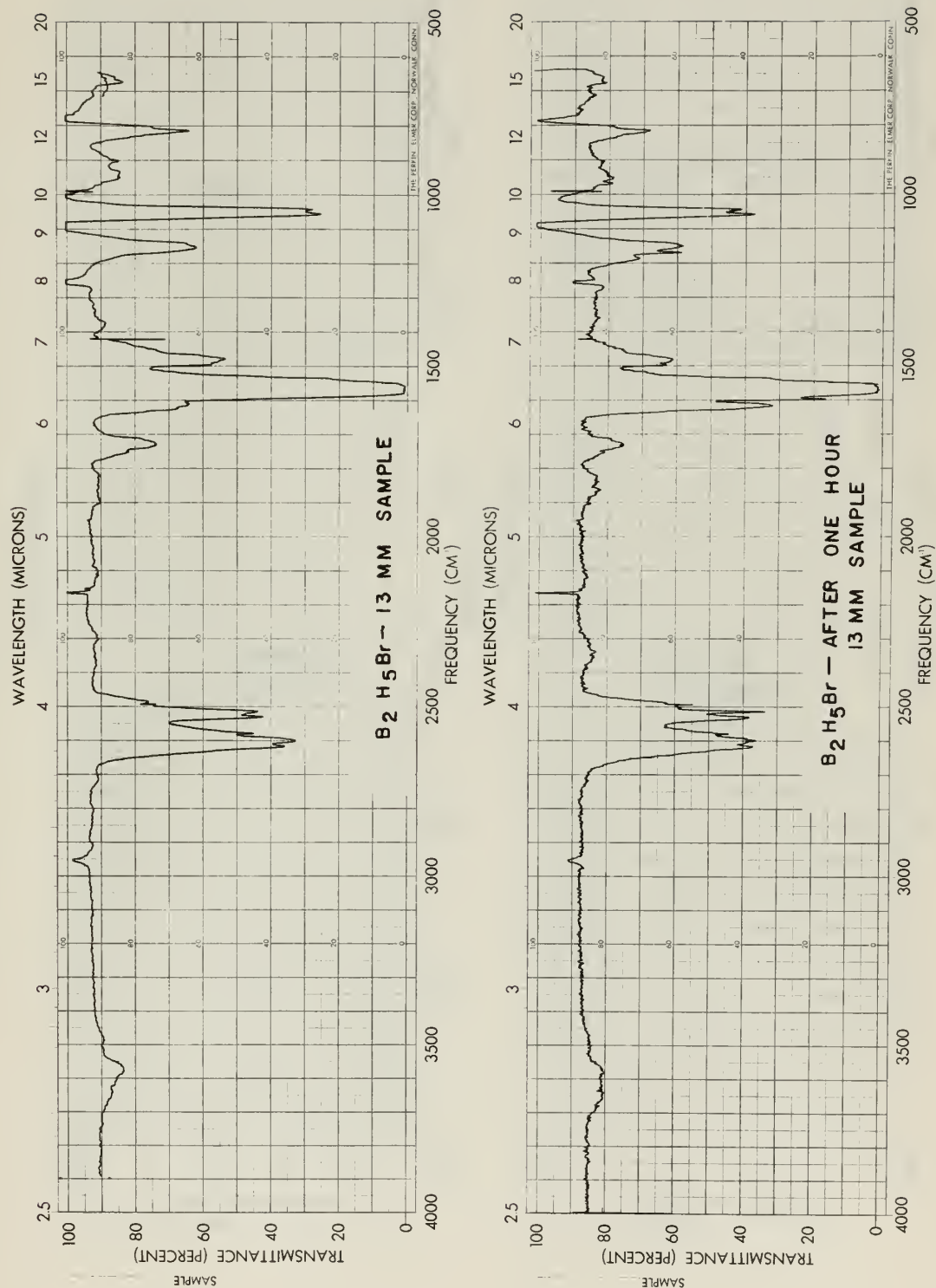


Fig. 3. Comparison of B<sub>2</sub>H<sub>5</sub>Br spectra when pure and after decomposing for an hour at room temperature.



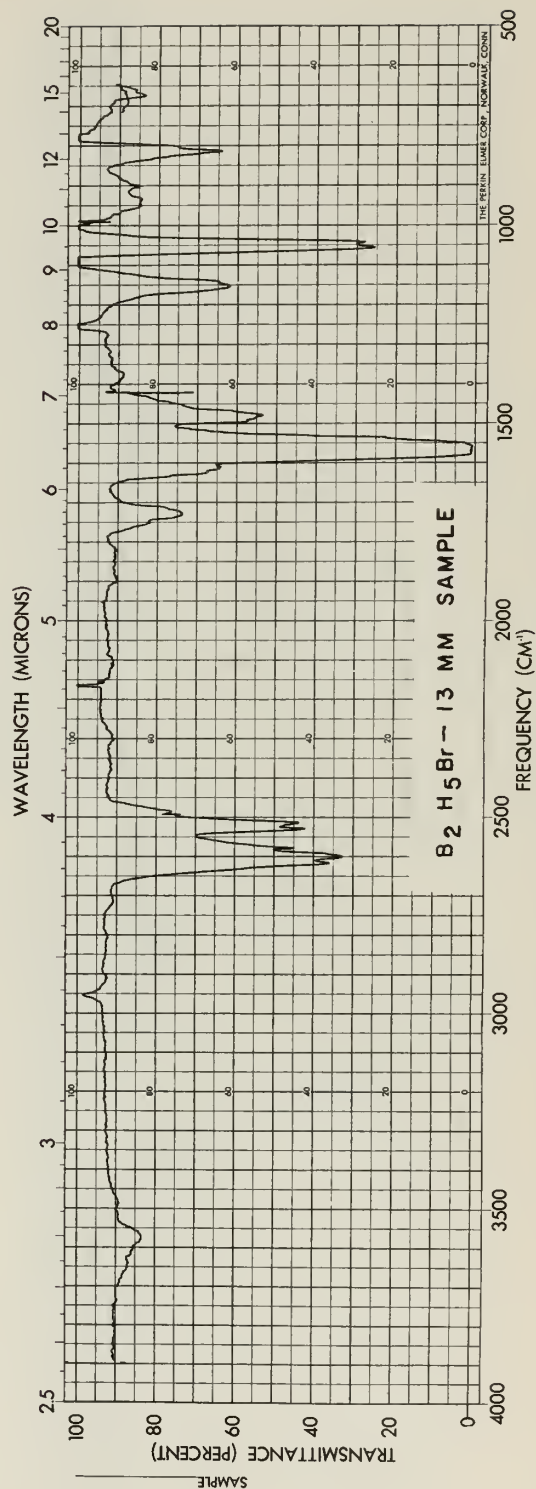
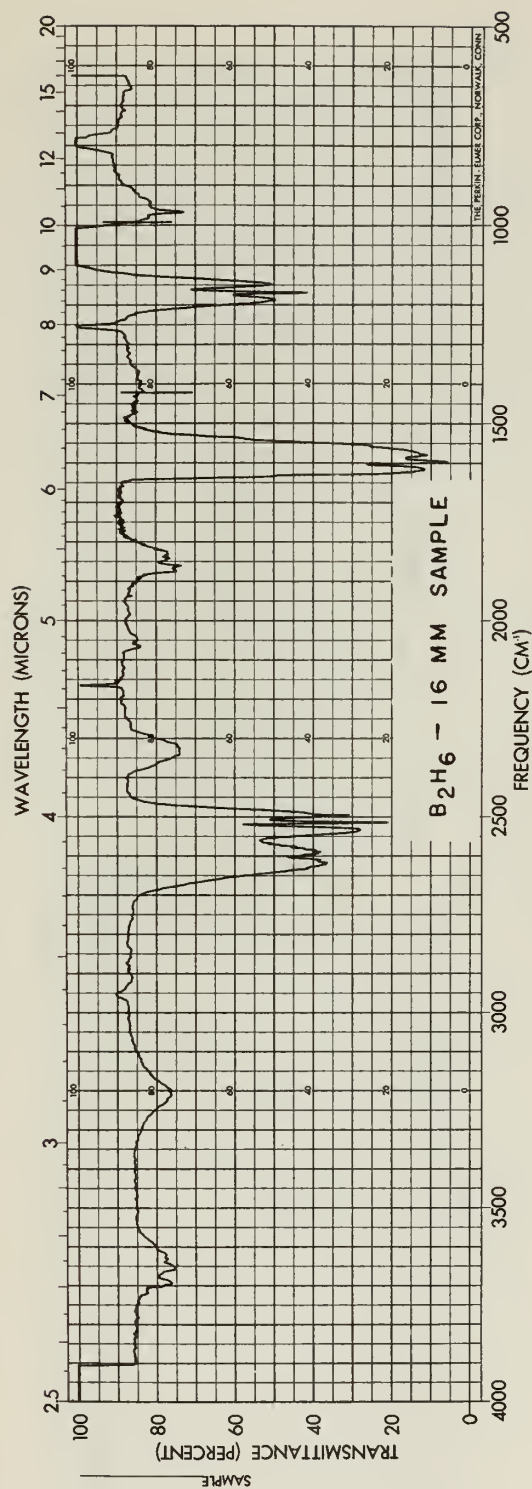


Fig. 4. Comparison of B<sub>2</sub>H<sub>6</sub> and B<sub>2</sub>H<sub>5</sub>Br spectra.







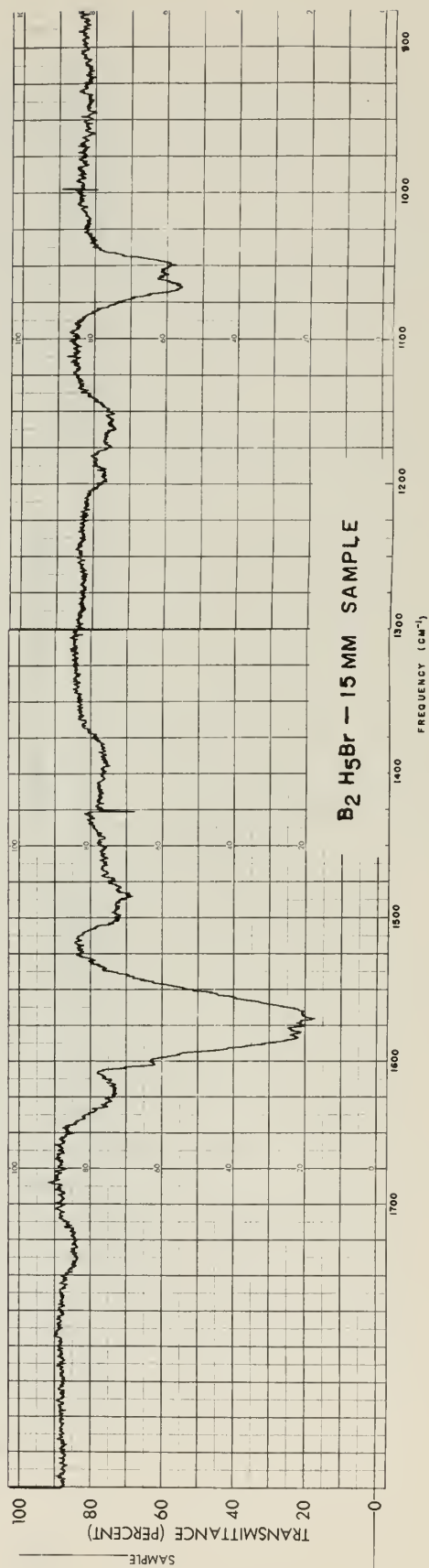
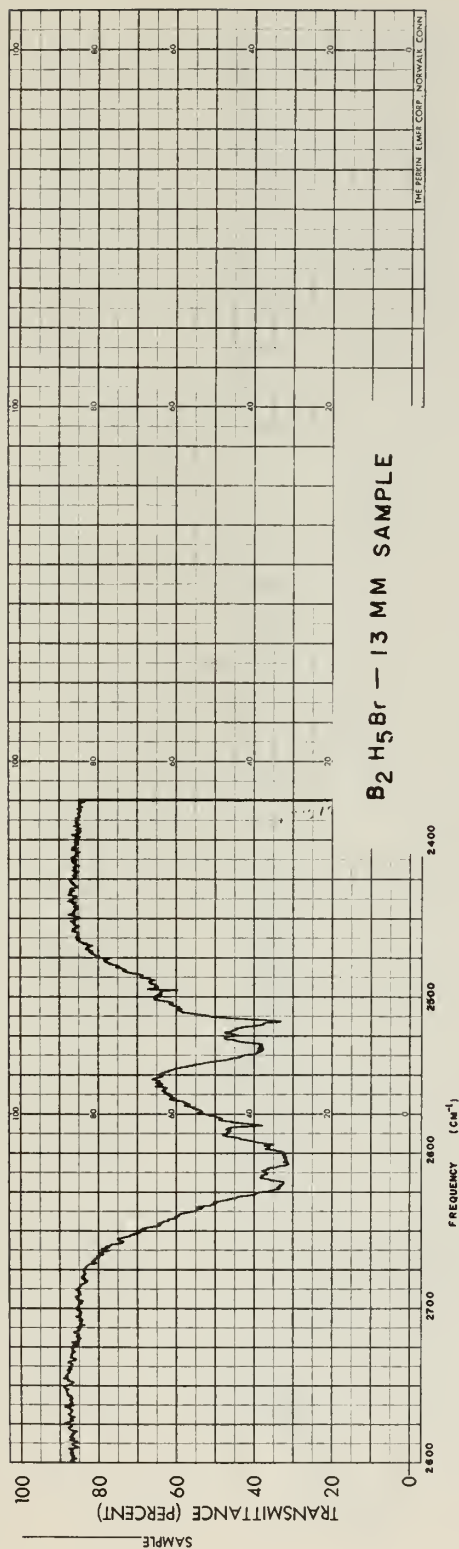


Fig. 5. B<sub>2</sub>H<sub>5</sub>Br spectrum on expanded scale.



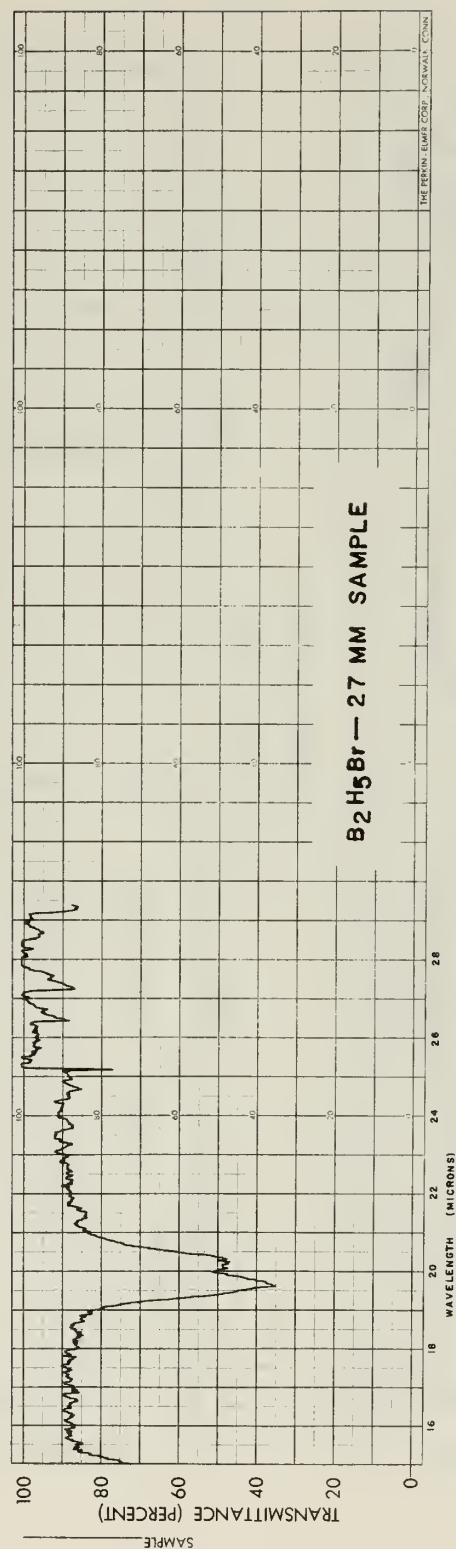
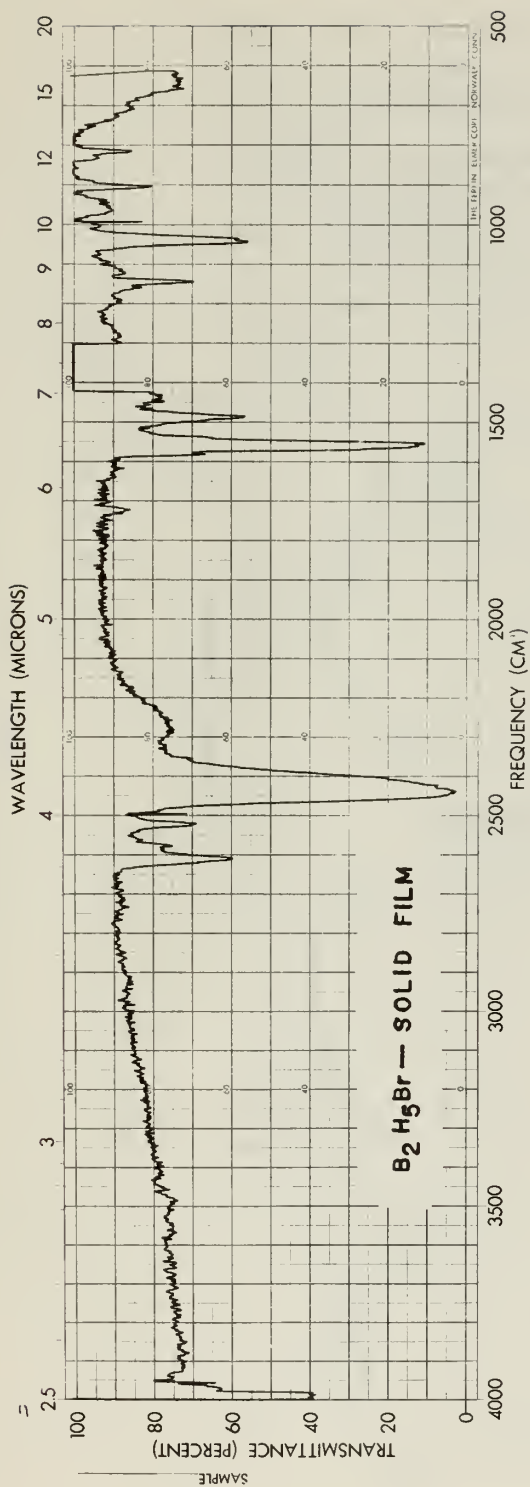
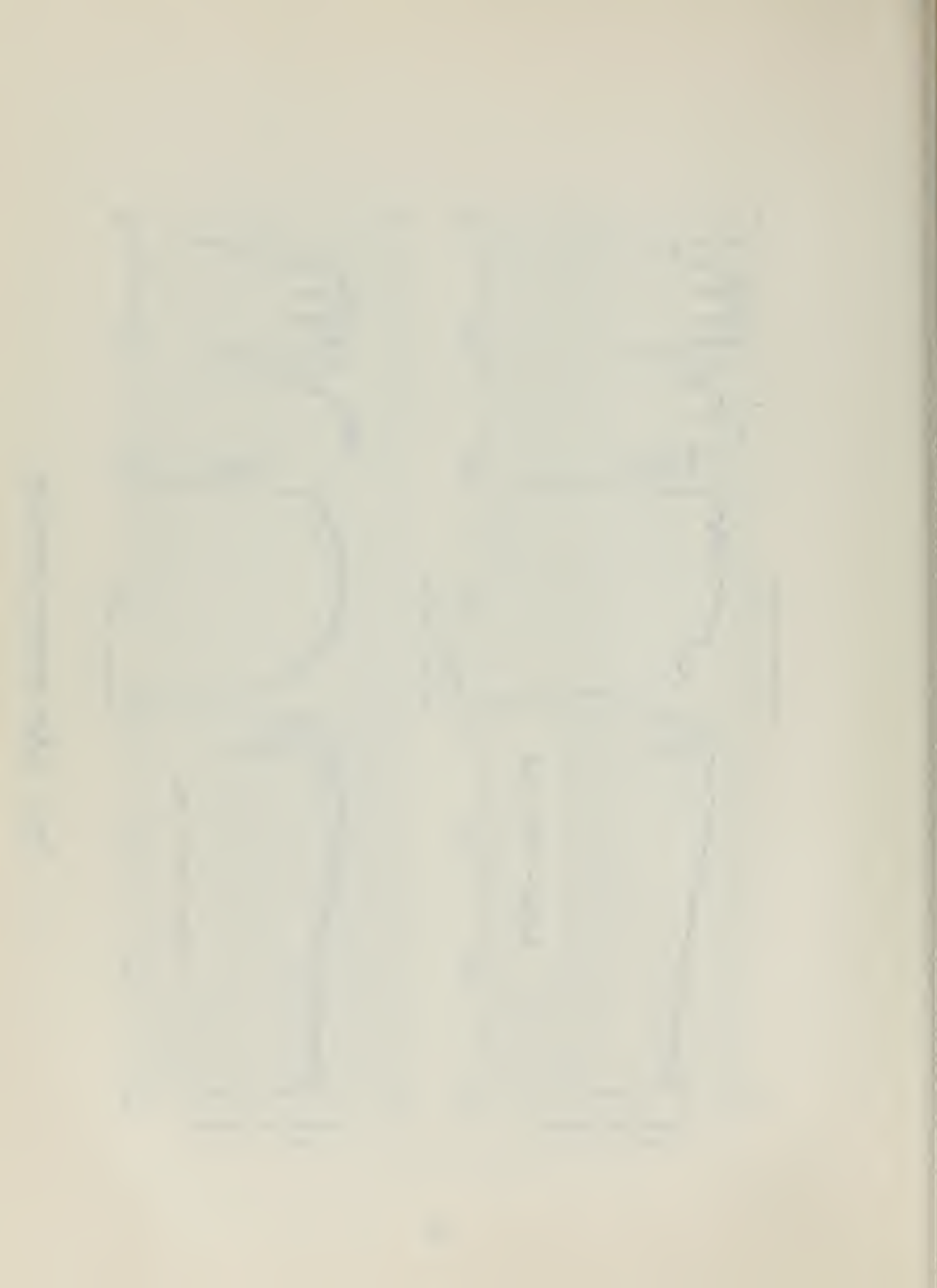


Fig. 6.  $B_2H_5Br$  spectrum in cesium bromide region.







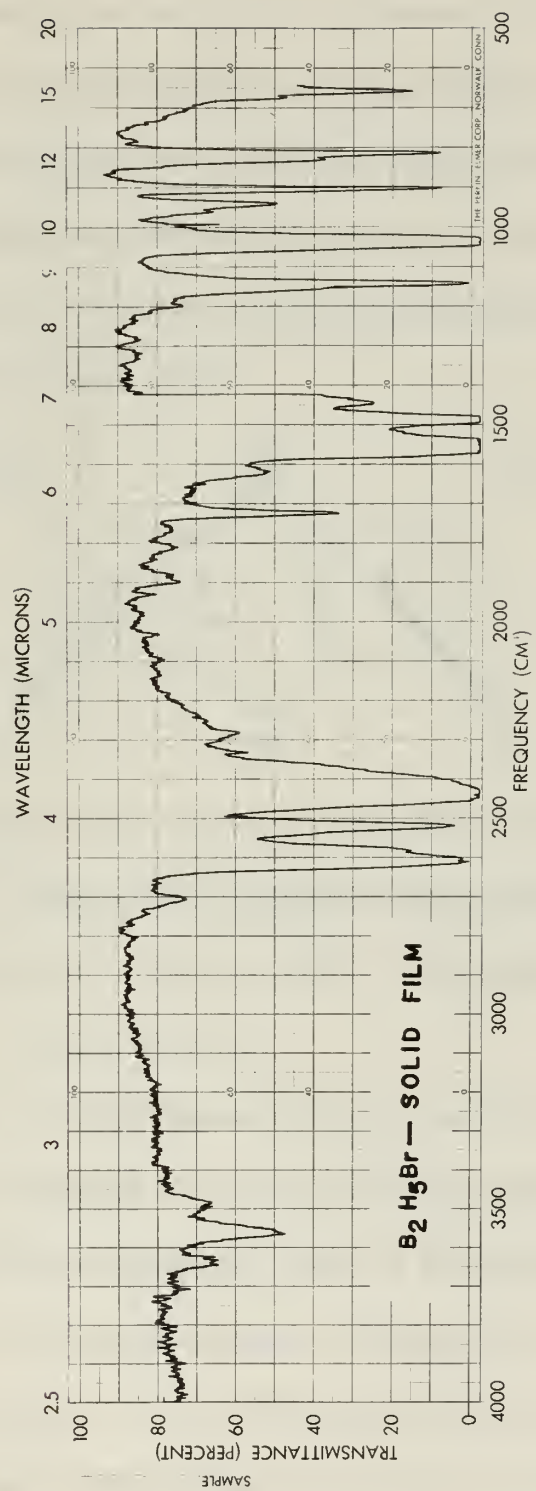
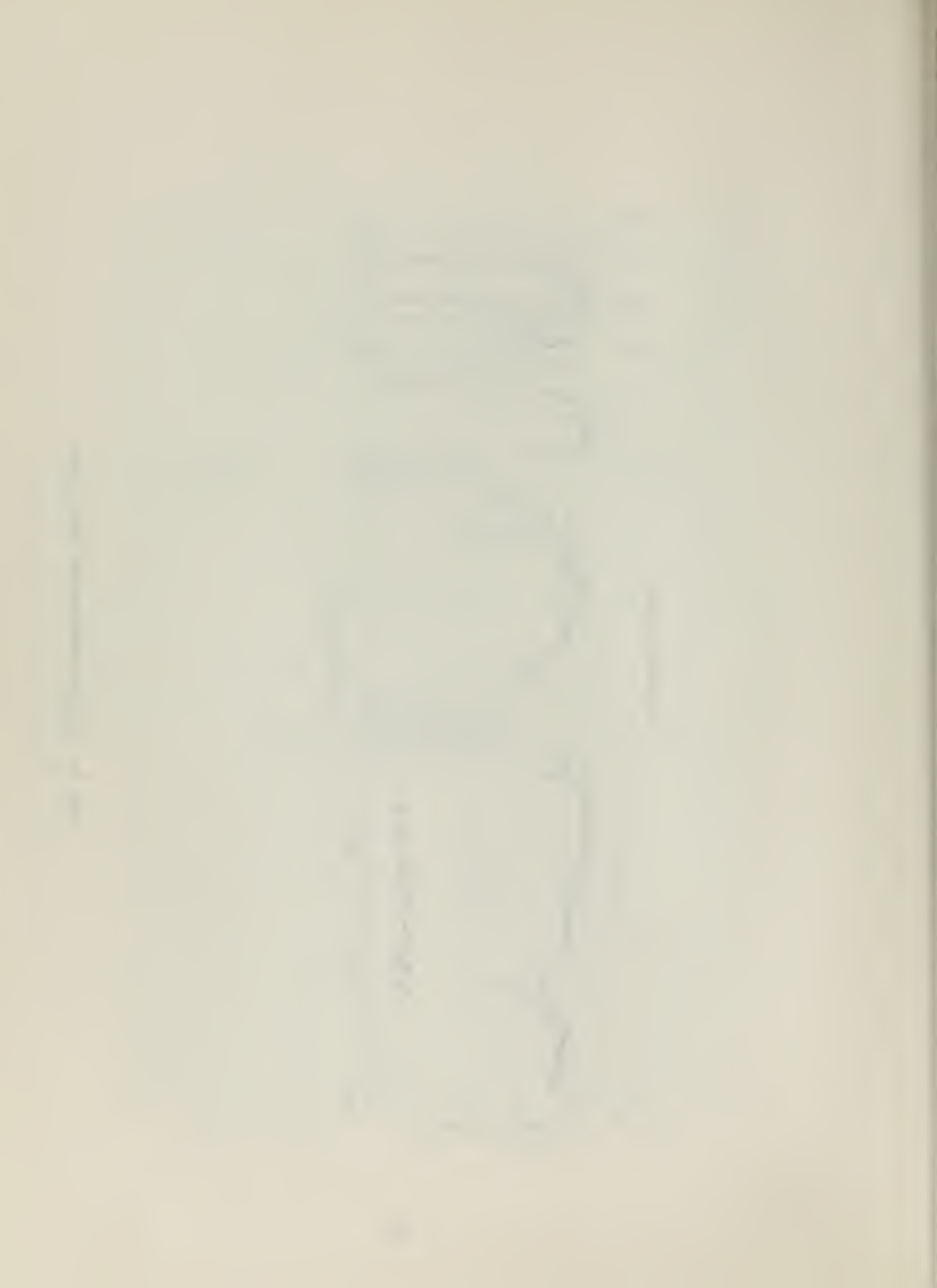


Fig. 8.  $B_2H_5Br$  spectrum as solid film.

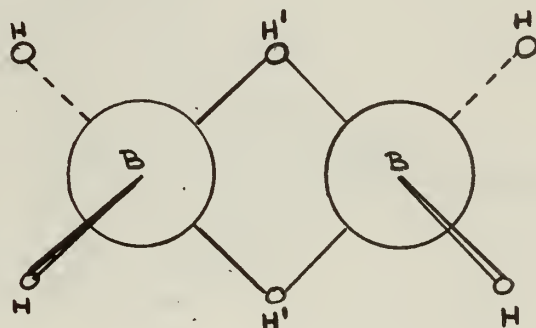




### III. INTERPRETATION OF INFRARED SPECTRUM OF $B_2H_5Br$

#### 1. Symmetry of $B_2H_5Br$ .

The presently accepted model of diborane /2/ is a bridge model in which two boron atoms and four terminal hydrogens lie in one plane while the same two boron atoms and the bridge hydrogens (designated  $H^0$ ) lie in another plane perpendicular to the first. The configuration is shown below. /14/ The molecular dimensions were obtained by a careful electron diffraction study. /15/



The hydrogen atoms with a ligancy of one, have a H-B distance of  $1.187 \pm 0.030^{\circ}A$ . The bridging hydrogen atoms with a ligancy of two, have a B-H distance of  $1.334 \pm 0.027^{\circ}A$ . The distance between the boron atoms is  $1.770 \pm 0.013^{\circ}A$ .

Since there are eight atoms in  $B_2H_6$ , the  $3N$  less six fundamental vibrations total 18 and are numbered according to Bell and Longuet-Higgins, /12/ and are illustrated in Fig. 9 and described in Table II.

Hedburg, Jones and Schomaker /16/ report the structure of bromodiborane,  $B_2H_5Br$ , as essentially identical with that of diborane, except that a bromine atom replaces one of the non-bridging hydrogen atoms. Therefore, the symmetry of  $B_2H_5Br$  is reduced to one plane



	Description	$B_2H_5Br$ Species	Band Type
1	B-H sym., in phase	$A'$	AB
2	B-H' sym., in phase (breathing)	$A'$	AB
3	HBH in phase	$A'$	AB
4	B-B (slight B-H' stretch)	$A'$	AB
5	$BH_2$ twisting, opposite direct.	$A''$	C
6	B-H' asym., out of phase	$A''$	C
7	$BH_2$ wagging (into-with out-of-plane)	$A''$	C
8	B-H asym., in phase	$A'$	AB
9	$BH_2$ rocking ( $\nearrow \searrow$ )	$A'$	AB
10	$BH_2B$ (4th power)	$A'$	AB
11	B-H asym., out of phase	$A'$	AB
12	$BH_2$ rocking ( $\nwarrow \swarrow$ )	$A'$	AB
13	B-H' sym., out of phase	$A''$	C
14	$BH_2$ wagging (both into plane)	$A''$	C
15	$BH_2$ twisting same dir. (with motion of H')	$A''$	C
16	B-H sym., out of phase	$A'$	AB
17	B-H' asym., in phase	$A'$	AB
18	HBH out of phase	$A'$	AB

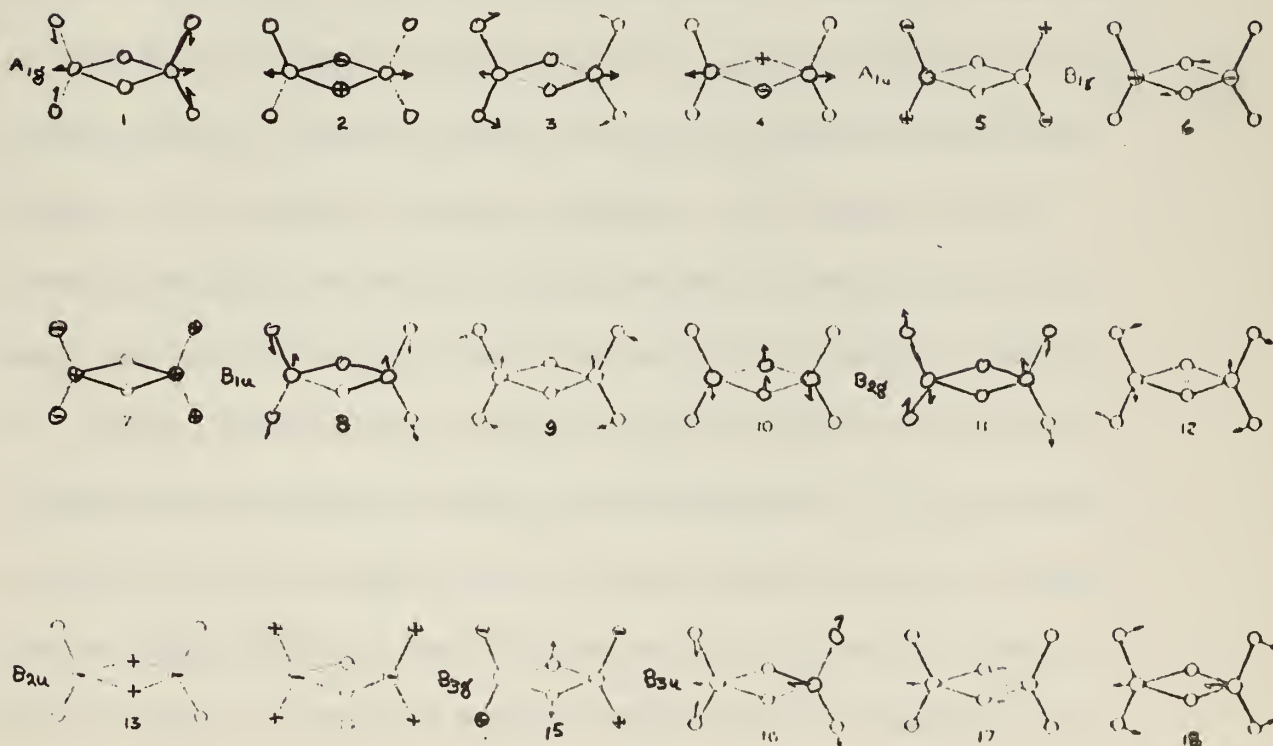


FIG. 9 The character of the normal vibrations of "bridge" diborane.  
(After Bell and Longuet-Higgins, 1957.)



(designated as symmetry point group  $C_s$  by Herzberg /13/) passing through the bromine, the two boron atoms and the remaining terminal hydrogens but passing perpendicular to the plane through the bridging hydrogens. There are only two vibrational species possible. Vibrations causing change of dipole moment within the plane of symmetry are species  $A'$ , and vibrations causing dipole changes out of the plane are species  $A''$ . /13/ All 18 fundamental vibrations for  $B_2H_5Br$  are infrared active. The 18 fundamental vibrations are composed of 12 $A'$  species and 6 $A''$  species. The symmetry relations for  $B_2H_5Br$  are also summarized in Table II.

There are three band types to be expected in the  $B_2H_5Br$  spectrum. Band type A refers to an absorption band in which there is a sharp center, Q branch, flanked by the nearly as intense P and R rotational envelopes. B-type bands refer to bands in which the center Q branch is absent and only the flanking P and R branches remain. Band type C refers to a band in which there is a sharp Q branch but no P or R branches are evident.  $B_2H_5Br$  is an asymmetric top type molecule, and change of dipole moment parallel to the axis of smallest moment of inertia, the minor axis, and in the plane of symmetry produces A-type bands of species  $A'$ . Dipole moment changes perpendicular to the minor axis and in the symmetry plane yield B-type bands, also of species  $A'$ . Out of plane vibrations producing dipole moment change parallel to the line through the two bridge hydrogens yield C-type bands of species  $A''$ . Some of the in-plane,  $A'$ , vibrations actually exhibit hybrid AB character. /5/





## 2. Frequency Assignments.

The spectrum of  $B_2H_5Br$  can best be analyzed by examining a small frequency range at a time utilizing the assignments given for diborane by Lord and Nielsen /1/ and correlating the expected shifts due to the terminal bromine with the shifts reported for  $B_2H_5D$  and  $B_2H_5CH_3$ . /5,6/ See Fig. 10 for a pictorial illustration of the correlation.

In diborane, the B-H (terminal) stretching vibrations ( $\nu_1$ ,  $\nu_8$ ,  $\nu_{11}$ ,  $\nu_{16}$  in Fig.9 ) are in the  $2500-2600\text{ cm}^{-1}$  region. Terminally substituted monodeuterodiborane and methyldiborane also show B-H stretch frequencies in this region. The asymmetrical stretch frequencies are higher than the symmetric and are located at  $2610\text{ cm}^{-1}$  for the in phase ( $\nu_8$ ) vibration and at  $2580\text{ cm}^{-1}$  for the out of phase ( $\nu_{11}$ ) vibration. The lower frequency symmetrical stretch band is found at  $2520\text{ cm}^{-1}$  in  $B_2H_5Br$ .

The B-H' stretching frequencies ( $\nu_6$  and  $\nu_{17}$ ) are found in the  $1750$  to  $1550\text{ cm}^{-1}$  region with the strongest band found in the region corresponding to the asymmetric, in phase,  $\nu_{17}$  in diborane. Thus  $1572\text{ cm}^{-1}$  is assigned to the asymmetric in phase B-H' stretch, and  $1730\text{ cm}^{-1}$  corresponds to the asymmetric out of phase B-H' stretch.

The fairly intense  $BH_2$  deformation bands reported at about  $1150\text{ cm}^{-1}$  for  $CH_3B_2H_5$  /5/ appear shifted to the lower frequency of about  $1050\text{ cm}^{-1}$  for  $B_2H_5Br$ . However, one apparent A-type band of medium intensity still remains at  $1155\text{ cm}^{-1}$  and probably corresponds to one of the  $BH_2$  deformation bands that did not shift appreciably.





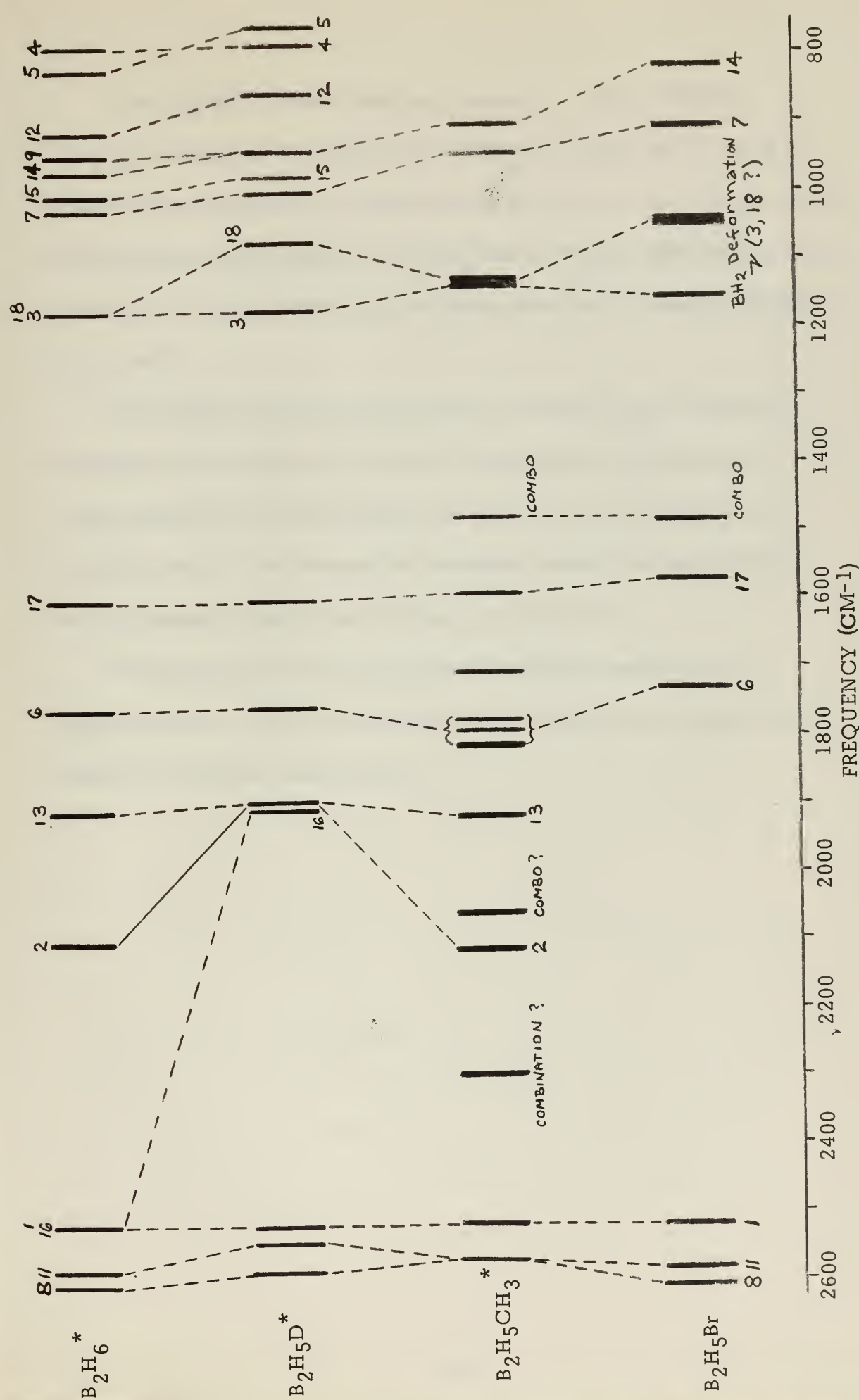


Fig. 10. Correlation of Frequencies for Terminally Substituted Diborane  
 \* Previously assigned by Lehmann, Ditter and Shapiro /5,6/



The  $\text{BH}_2$  out of plane wagging frequency, corresponding to  $\nu_7$  in  $\text{B}_2\text{H}_6$ , appears in the region from  $1000\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$ . It is a sharp C-type band of low intensity found at  $904\text{ cm}^{-1}$  for  $\text{B}_2\text{H}_5\text{Br}$ . The  $\text{BH}_2$  in plane wagging band, corresponding to  $\nu_{14}$  in diborane, is found at a slightly lower frequency as another sharp band of medium intensity at  $817\text{ cm}^{-1}$ .

Two other prominent bands stand out in the  $\text{B}_2\text{H}_5\text{Br}$  spectrum. The fairly intense band at  $1488\text{ cm}^{-1}$  corresponds well with the  $-\text{B}_2\text{H}_5$  combination band assigned as  $1481\text{ cm}^{-1}$  for  $\text{CH}_3\text{B}_2\text{H}_5$  /5/. The other band is the intense low frequency absorption expected for the B-Br stretch vibration and is found at  $496\text{ cm}^{-1}$ .

While there are other unassigned absorption peaks in the  $\text{B}_2\text{H}_5\text{Br}$  spectrum, further correlation with  $\text{CH}_3\text{B}_2\text{H}_5$  and  $\text{B}_2\text{H}_5\text{D}$  fails to yield any other firm assignments.



#### IV. DISCUSSION OF RESULTS

All the band assignments have been made using the spectrum of  $B_2H_5Br$  in the gas phase. The spectrum of  $B_2H_5Br$  in the solid phase is included for completeness, and it was quite useful in helping to determine whether a particular band was A-type or B-type. Although the Q branch is missing in the B-type band of a gas, the solid spectrum yields a simple peak at the vibrational frequency. Therefore, if there was little or no shift in frequency for a particular band when going from the gas phase to the solid phase, the type band was easily distinguishable. However, some of the bands do shift when in the solid phase as compared to the gas phase, and not all the bands could be determined as to type. Further infrared study of solid  $B_2H_5D$  and  $CH_3B_2H_5$  and correlation in the solid state might allow some more firm band assignments for the  $-B_2H_5$  fragment. No doubt some of the bands in the  $2200 - 2450\text{ cm}^{-1}$  region of the solid spectrum could be assigned by a correlation of the solid spectra.

There is a large jump in the mass of the terminally substituted group when going from  $-CH_3$  or  $-CD_3$  to bromine, and the correlation of band assignments in the gas phase is not completely straightforward throughout the spectrum. The chlorodiborane spectrum would be especially useful in completing the correlation since it is of intermediate mass relative to the methyl and bromo substituted diborane; however, the greater electronegativity of the chlorine would complicate





the correlation somewhat. Still the usefulness of an absorption spectrum of chlorodiborane warrants another attempt at its preparation.

The attempts at preparing chlorodiborane for IR study in this work were limited to mixing  $B_2H_6$  and  $BCl_3$  (or  $HCl$ ) at a total pressure of about one half an atmosphere. Preparation using the same techniques only pressures of at least an atmosphere might be more fruitful. Although the hope of separating the  $B_2H_5Cl$  from its dissociation and equilibrium compounds is remote, compensation for the  $B_2H_6$  spectrum could be accomplished readily by placing  $B_2H_6$  of near equivalent absorption strength in the reference beam of the spectrometer. The interference with the expected  $B_2H_5Cl$  spectrum due to the spectra of  $HCl$  and  $BCl_3$  would be minimal, and compensation for the  $B_2H_6$  alone should permit resolution of the  $B_2H_5Cl$  bands.





## BIBLIOGRAPHY

1. R. C. Lord and E. Nielsen, *J. Chem. Phys.* 19, 1-10 (1951)
2. W. C. Price, *J. Chem. Phys.* 16, 894-902 (1948)
3. A. N. Webb, J. T. Nen and K. S. Pitzer, *J. Chem. Phys.* 17, 1007 (1949)
4. W. E. Anderson and E. F. Barker, *J. Chem. Phys.* 18, 698 (1950)
5. W. J. Lehmann, J. F. Ditter and I. Shapiro, *J. Chem. Phys.* 29, 1248-56 (1958)
6. W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.* 32, 1088-93 (1960); *J. Chem. Phys.* 33, 590-7 (1960)
7. R. A. Turner, Jr., *Infrared Spectra of Bismuth Trifluoride and Chlorodiborane. Attempted preparation of Bismuth Hydride for Infrared Study*, Thesis, United States Postgraduate School, Monterey, California, (1962)
8. H. G. Weiss and I. Shapiro, *J.A.C.S.* 81, 6167-8 (1959)
9. A. Stock, *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N.Y. (1933)
10. H. I. Schlesinger and A. B. Burg, *J.A.C.S.* 53, 4321-32 (1931)
11. G. R. Seely, J. P. Oliver, and D. M. Ritter, *Anal. Chem.* 31, 1993-5 (1959)
12. R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc.* 183A, 357 (1945)
13. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Company, Inc., Princeton, New Jersey (1945)
14. W. Dilthey, *Z. Angew. Chem.* 34, 596 (1921)
15. K. Hedberg and V. Schomaker, *J.A.C.S.* 73, 1482 (1951)
16. K. Hedberg, M. E. Jones, V. Schomaker, *2nd Int. Congr. Cryst.*, Stockholm (1951)
17. L. Pauling, *The Nature of the Chemical Bond*, 3rd edition, Cornell University Press, Ithaca, New York, (1960)















thesP267

Infrared spectrum of bromodiborane and a



3 2768 001 98071 7

DUDLEY KNOX LIBRARY